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ABSTRACT

The properties of silicon dioxide have been studied extensively over the years. However, there still remain major unanswered questions regarding the nature of the optical spectrum and the role of excitonic effects in this technologically important material. In this work, we present an *ab initio* study of the optical absorption spectrum of alpha-quartz, using a newly developed first-principles method which includes self-energy and electron-hole interaction effects. The quasiparticle band structure is computed within the GW approximation to obtain a quantitative description of the single-particle excitations. The Bethe-Salpeter equation for the electron-hole excitations is solved to obtain the optical spectrum and to understand the spatial extent and physical properties of the excitons. The theoretical absorption spectrum is found to be in excellent agreement with the measured spectrum. We show that excitonic effects are crucial in the frequency range up to 5 eV above the absorption threshold.

INTRODUCTION

Quartz is a technologically important material whose optical, structural, and electronic properties have been measured accurately. We are primarily interested in explaining theoretically the experiment of Philipp [1], who measured the optical absorption spectrum of a wide variety of silicates including glass and alpha quartz. The optical absorption spectrum he measured for alpha quartz shows 4 distinct peaks in the energy range from 10 eV to 20 eV. The nature and origin of these peaks led to a thirty-year long controversy. Different theoretical methods and approaches [2, 3, 4, 5] have been used to explain the origin of these peaks. In the theoretical work of the past thirty years, one of two approaches has been employed, i.e. either the interband transition approach or the exciton approach. In the interband theory, the optical absorption is computed using the quasiparticle energies and wavefunctions as input while neglecting the electron-hole interaction. Chelikowsky and Schluter [2] use an interband theory with an empirical bandstructure. Xu and Ching [3] also use the interband theory, but compute the single-particle energies within the local density approximation (LDA). Both groups claim that only the first peak is attributable to excitons whereas the other higher-energy peaks correspond to Van Hove singularities in the joint density of states (JDOS). In the exciton approach of Pantelides [4] and Laughlin [5], the optical absorption spectrum of alpha quartz is computed using an approximate form of the two-particle Green's function parametrized by tight-binding parameters and a model electron-hole interaction. Pantelides and Laughlin disagree from each other as to the nature of the peaks, as the former claims that only the first two peaks are due to excitons and the latter claims that all four peaks are excitonic.

In this work, we use accurate *ab initio* methods to compute the quasiparticle bandstructure and the electron-hole interaction. From these calculations we are able to compute not only the optical absorption spectrum but also the exciton wavefunctions giving rise to the

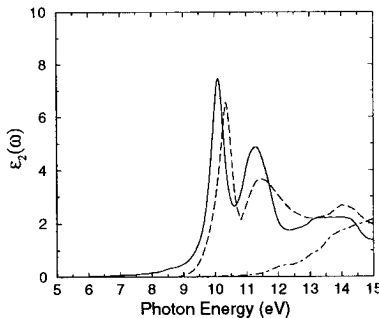


Figure 1: The absorption spectrum calculated with excitons (solid line), with the interband theory (dotted-dashed line), and experiment (dashed line) [1].

peaks in the absorption spectrum. Since we do not make any assumptions beforehand as to the nature of the excitons in alpha quartz, we are in a position to resolve the long-standing controversy as to the nature of the peaks.

THEORY

We compute the optical properties and optical excitations of alpha quartz using a method similar to that of Rohlfing and Louie [6], who have computed the absorption spectrum and exciton wavefunctions of a wide variety of semiconductors and insulators, including surfaces, clusters, and polymers [7, 8]. They have obtained excellent agreement with experiment for all such systems. Similar approaches with different theoretical and numerical methods have been used by others to study the optical properties of solids [9, 10]. Below, the formalism and approach used are briefly summarized.

Before computing the optical excitations and spectrum, a calculation of the quasiparticle energies, $\{E_{c\mathbf{k}}^{QP}, E_{v\mathbf{k}}^{QP}\}$, and wavefunctions, $\{\phi_{c\mathbf{k}}(\mathbf{r}), \phi_{v\mathbf{k}}(\mathbf{r})\}$, is performed. Here “c” and “v” are the conduction and valence band indices, respectively, and “k” is the k-point index. We compute the quasiparticle energies and wavefunctions using the Hybertsen-Louie approach [11] within the GW approximation [12].

The quantities of fundamental importance in the study of the optical excitations of a solid are the excitonic coefficients $A_{cv\mathbf{k}}$, which describe the coupling of the different free electron-hole pair configurations in the excited state. In particular, the effective two-particle exciton wavefunction in real-space can be obtained from the coefficients $A_{cv\mathbf{k}}$ through the following formula:

$$\Psi_s(\mathbf{r}_e, \mathbf{r}_h) = \sum_{cv\mathbf{k}} A_{cv\mathbf{k}}^{(s)} \phi_{c\mathbf{k}}(\mathbf{r}_e) \phi_{v\mathbf{k}}^*(\mathbf{r}_h). \quad (1)$$

The coefficients $A_{cv\mathbf{k}}$ are the eigenvectors of the following eigenvalue equation, known as the Bethe-Salpeter Equation (BSE) [13]:

$$(E_{c\mathbf{k}}^{QP} - E_{v\mathbf{k}}^{QP}) A_{cv\mathbf{k}} + \sum_{v'c'\mathbf{k}'} K_{cv\mathbf{k}, c'v'\mathbf{k}'} A_{c'v'\mathbf{k}'} = \Omega A_{cv\mathbf{k}}. \quad (2)$$

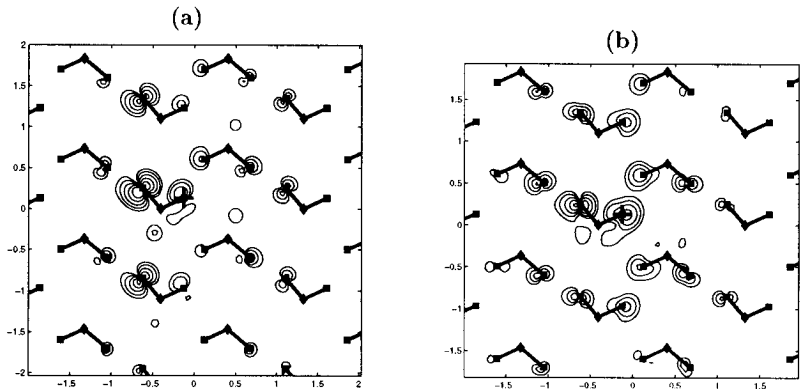


Figure 2: A log plot of the hole probability of (a) the dark exciton and (b) the first bright exciton with the electron placed at $+$. The plot is in the (110)-plane. The diamonds correspond to silicon atoms and the squares to oxygen atoms. The scale is in units of the lattice constant.

The eigenvalue Ω is the energy of the coupled electron-hole pair excitation, and $K_{cv\mathbf{k},c'\mathbf{v}'\mathbf{k}'}$ describes the scattering of an electron-hole in the configuration $cv\mathbf{k}$ to the configuration $c'\mathbf{v}'\mathbf{k}'$ via the Coulomb interaction. The kernel $K_{cv\mathbf{k},c'\mathbf{v}'\mathbf{k}'}$ is in general a complicated expression that may be expressed as an infinite sum over irreducible Feynman diagrams or as a sum of functional derivatives of the Hartree energy and electron self-energy. We take $K = 2K_x + K_d$, which is the appropriate expression for spin-singlet, optically-excitable states. Here, K_x is the exchange interaction and K_d is the attractive, screened Coulomb interaction between electron and hole. They are given explicitly by the following formulas:

$$K_{x,cv\mathbf{k},c'\mathbf{v}'\mathbf{k}'} = \int d^3r d^3r' \phi_{v\mathbf{k}}(\mathbf{r}') \phi_{c\mathbf{k}}^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{v'\mathbf{k}'}^*(\mathbf{r}) \phi_{c'\mathbf{k}'}(\mathbf{r}) \quad (3)$$

$$K_{d,cv\mathbf{k},c'\mathbf{v}'\mathbf{k}'} = - \int d^3r d^3r' \phi_{v\mathbf{k}}(\mathbf{r}) \phi_{v'\mathbf{k}'}^*(\mathbf{r}) W(\mathbf{r}, \mathbf{r}') \phi_{c\mathbf{k}}^*(\mathbf{r}') \phi_{c'\mathbf{k}'}(\mathbf{r}'), \quad (4)$$

where $W(\mathbf{r}, \mathbf{r}')$ is the screened Coulomb interaction in the static approximation. The optical absorption spectrum, $\epsilon_2(\omega)$, is given (in atomic units) by:

$$\epsilon_2(\omega) = \frac{4\pi}{\omega^2} \sum_s \left| \sum_{cv\mathbf{k}} A_{cv\mathbf{k}}^s \langle c\mathbf{k} | \mathbf{V} \cdot \hat{\mathbf{e}} | v\mathbf{k} \rangle \right|^2 \delta(\omega - \Omega_s), \quad (5)$$

where \mathbf{V} and $\hat{\mathbf{e}}$ are the velocity operator and the polarization vector, respectively.

RESULTS

We first compute the quasiparticle bandstructure in the GW approximation of alpha quartz. The nearly direct gap at Γ is opened up significantly, as expected, from the LDA value of 5.6 eV to a value of 10.1 eV.

We solve next the BSE for $A_{cv\mathbf{k}}$ and compute the optical spectrum using Eq. 5. Figure 1 shows the spectrum from 5 to 15 eV. The two theoretical peaks shown are located at 10.1

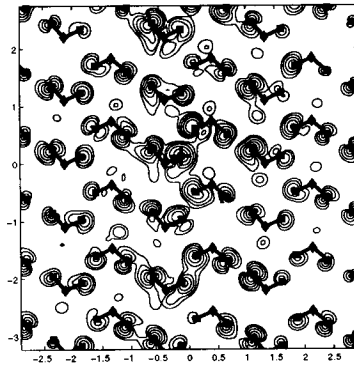


Figure 3: A log plot of the hole probability of the second bright exciton at 11.3 eV with the electron placed at $+$. The plot is in the (110)-plane. The diamonds correspond to silicon atoms and the squares to oxygen atoms. The scale is in units of the lattice constant.

and 11.3 eV, which agree quite well with the experimental values of 10.3 and 11.7 eV. We see that the first two peaks are clearly excitonic in nature, since the absorption without excitonic effects is nearly featureless in the interval from 0 eV to 15 eV. This resolves definitively the controversy as to the nature of the first two peaks, which cannot be explained by Van Hove singularities in the interband transition results. We have not included enough conduction bands in the BSE to be able to compute the last two peaks.

To illustrate the wave function of such excitations, we place the electron at a fixed point close to one of the oxygen atoms, and plot the probability of finding the hole on the (110)-plane. Noting the form of Eq. 1 and the fact that the highest valence bands are oxygen p-like in character, we expect the plot arranged in this way to show localized lone-pair p-orbitals on the oxygen atoms modulated by an envelope function characterizing the extent of the exciton. As shown in Fig. 2, the lowest energy excitation is a charge-transfer exciton which has a very small probability of hole and electron being in the same place. This accounts for the fact that this excitation is very weak. We also notice that this dark exciton is very localized. Fig. 2 shows the exciton wavefunction of the first bright peak. It is a fairly localized exciton and has a very high electron-hole overlap probability, consistent with the fact that it gives rise to a very sharp peak at 10.1 eV.

Fig. 3 shows the exciton corresponding to the second bright peak. It is a resonant exciton delocalized along the direction perpendicular to the hexagonal plane.

CONCLUSION

In conclusion, we obtain excellent agreement with the experimentally measured absorption to 5 eV above the absorption threshold. We find two bound excitons: one charge-transfer, dark exciton, which gives rise to the small shoulder in the optical absorption at 8.4 eV; and one bright exciton, which gives rise to the first sharp peak at 10.1 eV. We find that the second sharp peak at 11.3 eV is attributable to a resonant exciton whose spatial nature is very extended along one direction.

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